Contributions from the Laboratory of the University of Pennsylvania.

No. VII.

On astrophyllite, arfvedsonite and zircon, from El Paso Co. Colorado, and a colorimetric estimation of titanium before the blow-pipe.

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General occurrence. The three minerals are imbedded in quartz. On the specimens which I examined no orthoclase, nor any other species could be found ; yet the mother rock may be presumed to be a very coarse grained granite or syenite. Until satisfactory information is received on this point, it must, of course, remain doubtful. In stating that the three minerals occur together, it is but right to say, that I make a hearsay statement.
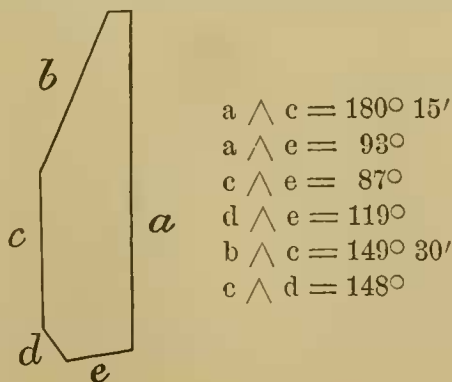
For, the specimens of quartz in which astrophyllite and zircon abound, are destitute of arfvedsonite, and the specimen on which the latter is abundant, does not show either of the two other species. But the character of the quartz, as the common matrix, is strictly identical throughout, of grayish color, locally stained with iron ochre, and massive in structure. The co-occurrence of these three species, at once calls up the close similarity with that of Brevig in Norway, the only locality at which astrophyllite was known to exist. The only difference being that orthoclase forms the matrix at Brevig, and quartz in Colorado.

To Dr. Foote, of this city, I am indebted for the material of this investigation.

I. Astrophyllite.

Geometrical properties. The crystals exhibit elongated prismatic forms, the cross section being nearly a rectangle on the majority of the individuals. I succeeded in finding some crystals, however, whose section is more complicated and with which I endeavored to establish the angular relations between the several faces. No terminal development of any kind could be observed ; the crystals appear all broken across the direction of main extension.

The measured edges are, therefore, all in one zone. The figure represents a cross section of the best developed crystal, and the faces are designated a, b, c, etc., solely in reference to their sequence.

$$a \wedge c = 180^\circ\ 15'$$
$$a \wedge e = \ \ 93^\circ$$
$$c \wedge e = \ \ 87^\circ$$
$$d \wedge e = 119^\circ$$
$$b \wedge c = 149^\circ\ 30'$$
$$c \wedge d = 148^\circ$$

a is a cleavage face and reflects a sharp image, the other faces are true crystal faces, and, with the exception of e, reflect very imperfectly. The largest face (a) is not quite one-eighth of an inch wide. The measurement does not make any pretension of scientific accuracy for the reasons stated, yet the above angles are the means of repeated observations, which only differed by 1°, for the edges a ∧ e, e ∧ e, and by less than 30′ for the other edges. Their approximate accuracy taken for granted, they clearly admit only an interpretation according to the laws of the monosymetric system, when c becomes the basal plane, e an orthopinakoid, b and d hemi-domes.

Scheerer, who first described the species (B. II. Ztg. XIII 240, 1854) arrived at a different result. His measurements lead to an orthorhombic interpretation, and the optical investigations of Des Cloizeau (Dana, mineralogy) corroborate his view. But as none of the angles measured by me, find and analogon in those given by Scheerer, no comparison can be made, and future study must decide the truth.

Structural properties. A very marked cleavage exists parallel to the face c, by which the structure becomes eminently micaceous. The cleavage is indicated on the lateral faces by a decided striation (very plainly visible on the quartz, after the removal of crystals), and re-entering angles. Unlike other micaceous minerals, the laminæ are but very slightly elastic and tenacious, being easily reduced to a fine powder. That the crystals break easily across the main extension has already been mentioned. Hardness about 3.

Optical properties. Color from brass yellow to deep bronze brown. Transmitted light deep yellow to reddish brown. Appearance of the powder at a certain degree of fineness like mosaic gold. I could not obtain an image of interference with a lamina, through which types of ordinary print were plainly visible. But not possessing much experience in optical investigation, I have referred it to Professor P. Groth, of Strassburg.

Specific gravity $= 3.375$ at 15 C°.

Pyrognostic properties. The mineral fuses very readily to a black globule in the flame of an oil lamp. With microcosmic salt the reactions for iron, manganese, titanium and silica are easily obtained.

The mineral decomposes completely with sulphuric acid at ordinary pressure, and very readily in a sealed tube at 140 C°.

Composition :

			Oxygen.		
SiO_2	=	34.68	18.485	⎫	
TiO_2	=	13.58	5.299	⎬	24.363
ZrO_2	=	2.20	0.579	⎭	
Fe_2O_3	=	6.56	1.968	⎫	2.294
Al_2O_3	=	0.70	0.326	⎭	

Oxygen.

$$
\begin{array}{lll}
FeO &=& 26.10 \quad 5.799 \\
MnO &=& 3.48 \quad 0.784 \\
K_2O &=& 5.01 \quad 0.851 \\
Na_2O &=& 2.54 \quad 0.655 \\
MgO &=& 0.30 \quad 0.120 \\
CuO &=& 0.42 \quad 0.047 \\
TaO_5 &=& 0.80 \\
H_2O &=& 3.54 \quad 3.147 \quad \} \quad 3.147
\end{array}
$$

$\left. \begin{array}{c} \\ \\ \\ \\ \\ \end{array} \right\}$ 8.256

———
99.91

The oxygen ratio becomes :

$$\ddot{R} \; : \; \dddot{R} \; : \; \dot{R} \; : \; \dot{H} .$$
$$32 \; : \; 3 \; : \; 11 \; : \; 4 .$$

$$(H_2O)_4 \quad \left[(Si\ Ti\ Zr)\ O_2 \right]_{16} \quad \left[(Fe_2\ Al_2)\ O_3 \right] \quad \left[(Fe, K, Mn, Na,)\ O \right]_{11} .$$

To obtain the atomistic symbol, we have :

				Quotients.	Atoms.
Si	=	16.195	: 28	0.578	13.13
Ti	=	9.281	: 50	0.185	4.25
Fe	=	5.090	: 112	0.044	1.00
Fe	=	20.331	: 56	0.363	8.25
Mn	=	2.696	: 55	0.049	1.11
K	=	4.159	: 39	0.107	2.43
Na	=	1.885	: 23	0.081	1.84
H	=	0.393	: 1	0.393	8.93
O	=	38.060	: 16	2.379	54.07

The most rational approach to these figures will be represented by the symbol

$$
\left. \begin{array}{ccc}
\overset{IV}{Si_{13}} & \overset{IV}{Ti_4} & \\
\overset{''}{Fe_8} & \overset{VI}{Fe} & \overset{''}{Mn} \\
K_3 & Na_2 & H_{10}
\end{array} \right\} \quad \overset{''}{O_{54}}
$$
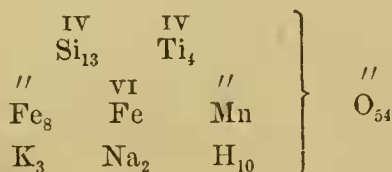
by which all the affinities are satisfied.

Note.—In the above calculation zirconium is converted into its equivalent of titanium, aluminum into ferric iron, magnesium and copper into the bivalent ferrous iron. Tantalic acid was left out, partly because its existence in the mineral is *not* established beyond doubt, and also because the general features of the formula would not be altered by its introduction.

Comparing my analytical results with those of Pisani, Scheerer, et. al. who analysed the Brevig mineral (Dana, mineralogy, ed. 5, 309), whilst a general conformity appears evident, there exists a difference in the percentages of titanium, aluminum and manganese too great to be passed in

silence. To facilitate the comparison, the results of the several analyses are placed side by side :

	Pisani.	Scheerer.	Meinecke.	Sieveking.	König.
Ti O_2	7.09	8.24	8.84	8.76	13.58
Zr O_2	4.97	——	——	——	2.20
$Al_2 O_3$	4.00	3.02	3.46	3.47	0.70
Mn O	9.90	12.63	12.68	10.59	3.48

Excepting Pisani's analysis, there is such close agreement between the others as could only be accounted for by an identical material and the following of precisely the same methods of analysis under the same circumstances. For, if Pisani's analysis is correct, there must be a variation in the composition of the Brevig mineral. Adding the percentages of Ti O_2, Zr O_2, $Al_2 O_3$ in Pisani's analysis, we obtain 16.06, against 16.48 in my analysis, whilst those sums in the other analyses are 11.26, 12.30, 12.23 respectively. But in regard to manganese, it seems evident that the mineral from Brevig and that from Colorado differ considerably, being only one third in the latter of that in the former.

It was stated above, that the astrophyllite is closely associated with zircon, which occurs in all sizes from $\frac{1}{4}$ inch to microscopic size. After the astrophyllite has been picked with all possible care, and is reduced to powder in a mortar, an occasional harsh grit is noticed. This suggests the intimate admixture of a hard, granular mineral, probably zircon, and the zirconia found by analysis might only be derived from admixed zircon. To test this question I decomposed the mineral with sulphuric acid of medium concentration, filtered from the insoluble, and digested the residue with sodium hydrate. A white, sandy residue, of great hardness, was obtained, ranging from 3 to 6 per cent. in different samples. I analysed it by itself, and found it to be a mixture of quartz and zircon. Since zircon, even as finest powder, is not acted upon sensibly by sulphuric acid of medium concentration, and as I had avoided the crushing of the hard grains as much as possible, I feel confident to assert that whatever zirconia was found in the sulphuric solution was in molecular combination as astrophyllite, and not derived from admixed zircon. By the same process I made sure that no titanium was present in the form of rutile or titanite, or any other titanium mineral.

I proceed now with the description of a method for the qualitative and quantitative determination of titanium, zirconium and aluminum, which I believe to be new and especially serviceable when the quantity of the mixed metals is very small. The best method for separating titanium from aluminum is stated to be (Rose, quant. analysis   ) the boiling of the dilute sulphuric solution, when titanium dioxyhydrate will precipitate. This is only relatively true, depending on the relative quantities of metals and of salts in the solution. If the solution be strongly acid, titanium is not completely precipitated, and in certain cases not precipitated at all. (A detailed account of the behaviour of titanium, zirconium and aluminum

will be published hereafter in connection with the reactions of the problematic earth in schorlomite.) If the solution be very neutral, a large percentage of aluminum is precipitated. Owing to this behaviour, titanic dioxyd is often given as alumina, and *vice versa*. When the ferric oxyd, after the supposed precipitation of titanium, is weighed, re-dissolved and estimated by permanganate, the deficit is considered to be alumina, when in reality it is titanium, or zirconium dioxyd. However, my method although applicable to large quantities is more especially designed for small residues, with which precipitations, for physical and chemical reasons, give rise to considerable error.

The mixed oxyds are digested with equal parts of water and concentrated sulphuric hydrate at increasing temperature, until the excess of acid is evaporated. I dissolve now in the smallest possible quantity of water, and bring the liquid upon a watch glass, where a quantity of diammonium sulphate is added, corresponding to the alum equivalent of alumina equal to the weight of the mixed oxyds. A gentle heat is applied until the ammonium salt is dissolved, and the whole is allowed to evaporate spontaneously in a warm place. Under these conditions, titanium, zirconium and aluminum form double salts with ammonium, but those of the two former are very soluble in cold water; while the well-known aluminum double salt, the alum, partly owing to the physical conditions of the crystals, is only slightly soluble in cold water, and still less so in a solution of ammonium or potassium sulphate. Accordingly, the dry mass of salts is moistened with a few drops of cold water, when every salt, but the alum will pass into solution, and the latter salt will be recognized at once, under the lens, by peculiar and constant octahedric forms.

This salt is so granular, that it can readily be freed from accompanying salts by decantation, washing with a solution of ammonium sulphate. Comparative tests showed that this washing process may be continued at length, without effecting a perceptible decrease of the alum. Thus freed from its mother liquor, the crystals may be removed into a small platinum crucible by means of a small piece of filter paper, ignited over the blast lamp, aluminum sesquioxyd obtained in great purity, and its weight ascertained. If the quantity be very small (less than 0.0005 gr.) the filter paper, whose ashes bring in impurity, the crystals may be washed into the crucible with a small amount of boiling water. In this manner I could estimate 0.0001 gr. and obtain a very distinct confirmative test by cobalt nitrate, before the blow-pipe. Experiments demonstrate that the presence of titanium and zirconium sulphates does not interfere with the complete crystallization of aluminum as alum, and as this salt only contains eleven percentum of aluminum sesquioxyd, the sensitiveness of the reaction is readily understood.

Note.—The mixed oxyds must be freed from silica, which is easily accomplished by adding a drop or two of hydrofluoric acid, during their digestion with sulphuric acid.

I am well aware that the determination of aluminum as alum is not new,

but I have nowhere in the literature noticed a recognition of its superiority over other methods, and especially none applying to this separation from titanium and zirconium in a micro-chemical sense.

The mother liquor from the alum, containing the sulphates of titanium and zirconium, besides a considerable amount of ammonium sulphate, is evaporated in a platinum capsule (one with a conical apex preferable, as it facilitates the removal of the oxyds after ignition), evaporated to dryness and ignited with caution over a blast lamp. The oxyds are then left in a scaly condition, very finely divided and well adapted to the subsequent treatment. They might be precipitated by ammonium hydrate and then ignited; but this would cause some inevitable loss, and on the other hand silica would be again introduced by the filter ashes and from the glass vessels, which would interfere with the reactions. The oxyds would be obtained in hard pieces, requiring grinding, and augment the expenditure of work and time generally.

The difficulty, nay, impossibility, of separating titanium from zirconium is well understood by all analysts who have occupied themselves with the subject. I have not overcome these difficulties, but I hope being able to show my co-laborers a way by which a quantitative estimation of the two metals may be arrived at where they occur together. It was proposed already by the great Nepom. Fuchs to reduce titanium dioxyd or chlorid to the sesquichlorid by tin, and estimate its quantity volumetrically. Owing to the unstable nature of the sesquichlorid and other causes not understood, this method fails to give satisfaction. It is also proposed to effect a separation by boiling the acetate solution of the metals. In my experiments I have not been able to obtain anything like constant results, and the difficulty to remove the alkaline salts from the hydratic oxyds, causes errors in small quantities of the oxyds, amounting to twenty-five per cent.

In my prolonged working with titaninum and the earth of schorlomite, I had occasion to produce the blow-pipe reaction many hundred times, and noticing the various shades of color produced with microcosmic salt in the reducing flame, together with their constancy, I conceived the idea to make this reaction the basis of a quantitative colorimetric method. In the first instance it should be useful in determinative mineralogy to distinguish between the several titanium minerals, where a difference of 10 per cent. even would be sufficient to characterize a species. In working up the idea, however, I was astonished to see how rapidly the eye became sensitive to discriminate between the shades and intensities of color on small surfaces. Thus, when analyzing the astrophyllite, more minute and careful experiments proved that a very satisfactory quantitative estimation of titanium dioxyd may be effected when it is mixed with zirconium or other colorless oxyds, which themselves do not produce a coloration with microcosmic salt in the reducing flame. There are but three metals whose presence in even a comparatively small amount will interfere with the accuracy of this method : vanadium, chromium and tungsten. The two former produce a green salt in the reducing flame, the latter a deep sky blue.

I called attention to the effect of vanadium on the titanium reaction some time ago (Proceedings Acad. Nat. Sciences, March, 1876), when it was stated that the two metals, producing complimentary colors—red and green—will extinguish each other ; vanadium, however, may be recognized by its deep yellow color in the oxydizing flame, which is most intense at low temperature, while the yellow of titanium only shows at high temperature, just below red heat.   This point is not only of general interest, as a case which might possibly present itself to the analyst, but is of direct practical importance, since I have found vanadium in all the titanium minerals of Magnet Cove (Proceedings Acad. Nat. Sciences, March, 1876), and became aware of its existence just by applying this colorimetric method, to the small residues obtained from the iron sesquioxyd, by means of citric acid and ammonium sulphide.   Here the titanium had escaped precipitation by boiling, and would have been called alumina, since it formed a nearly white powder and did not give the amethyst red color in the reducing flame.   However, vanadium and chromium may be removed from the oxyds by fusion with potassium or sodium nitrate, a treatment which should never be omitted, if the highest degree of accuracy is desired in analysis.

Practical execution of the method.   I prepare titanium dioxyd and aluminum sesquioxyd, the former from rutile, the latter from alum, in the finest possible division, by igniting their respective ammonium citrates or tartrates, removing at the same time the last trace of iron by ammonium sulphide.   In this fine condition the oxyds are very readily dissolved by the acid sodium phosphate before the blow-pipe.   I then weigh out 0.1 gr. ; 0.095 gr. ; 0.090 gr. ; 0.085 gr.........0.005 gr. of each of the oxyds, and mix them together inversely by very careful trituration in the mortar. . I produce thus one series containing in

TiO_2	Al_2O_3
100	0
95	5
90	10
85	15
⋮	⋮
0	100

These twenty samples, of one decigramme each, I put in well corked glass tubes with their respective number ; they form the standard. 0.002 gr. of the standard mixture, and an equal weight of the unknown mixture are dissolved in equal quantities of microcosmic salt.   For very accurate determination it is necessary to weigh the salt (0.12 gr.), but with some experience it is sufficient to form a circular loop on the platinum wire one-eighth of an inch in diameter, then to add gradually of the salt until the bead is nearly spherical, possessing one-eighth inch thickness.   I use a guage for this purpose formed of two pins, whose points are one-eighth

inch apart, and between which the bead is made to pass with slight friction.
In order to dissolve the entire 2 milligrs., I bring the powder from the
scale pan on a square piece of Swedish filter-paper quarter inch square,
and place this upon a dark polished surface (bottom of an agate mortar).
With the last particles of the oxydes the paper is made to adhere to the
bead, burnt and thus no loss is possible. I keep a series of ten beads (from
10–10 per cent.) hermetically sealed in a glass tube for a primary com-
parison, and having thus established approximately the position in the
scale, it is easy to select one directly above and another below, with which
to compare. Any person accustomed to make colorimetric observations
with liquids will be able to use this method at once, without any special
practice. As the reflection from the spherical surface interferes to a cer-
tain extent with the adjustment of the color in the scale, I prefer flattening
the beads upon a heated steel anvil with a polished hammer, also heated,
to prevent a too rapid chilling of the glass.

The thickness of the wire determines the thickness of the glass. I place
the several glass plates alongside each other upon a flat porcelain slab, by
which means the slightest difference in shade and depth may be recognized.
The intensity of color is much greater towards the pure titanium than
towards the zero ; the blue rays being entirely absorbed by the glass at
25 p. TiO_2, the glass being then purely pink. I am now experimenting
upon the feasibility of extinguishing the color of the titanium by a gradu-
ated scale of green, representing per cent of titanium, by which means I
am led to believe this colorimetric method, before the blow-pipe, will be
made easier and more perfect.

2. Arfvedsonite.

Crystallographical properties. The crystals are elongated prisms with
the clinopinakoid. As the faces are of equal width the cross section forms
an equilateral hexagon. No terminal faces could be observed. The
obtuse prismatic angle was found 124° 30′ with the hand goniometer. The
habitus is altogether like that of common hornblende. In one large crystal,
which I obtained loose, measuring nearly 4 inches in length by one inch
in width, I noticed a disaggregation similar to that observed in uralite,
that is to say, the crystal breaks up, or crumbles into an infinite number
of small individuals. The principal direction of this parting appears to be
a plane parallel to the orthopinakoid, a face not developed in the crystal.
These small individuals exhibit brilliant faces and give a prismatic angle
of 124° 5′ on the reflexion goniometer. On the smaller and more compact
crystals, which are imbedded in quartz, I observed a cleavage parallel to
the orthopinakoid quite as marked as that parallel to the prism. I could
not measure the angle accurately, but it appeared larger than the angle of
the prism. The *color* is raven black (after removing superficial impurities
by hydrochloric acid), the *lustre* submetallic, and the color of fine powder
is lavender blue.

Hardness = 6.

Specific gravity = 3.433 at 12 C° (with coarse powder). *Before the blowpipe* melts easily to a black glass in the flame of oil lamp. With microcosmic salt gives the reaction of silica, iron, manganese, and with difficulty that of titanium. Colors the flame yellow. Imperfectly decomposed by fusion with K H S O$_4$, not acted upon by hydrochloric and sulphuric acid at atmospheric pressure, and very slowly decomposed with sulphuric acid in a sealed tube at 160 C°.
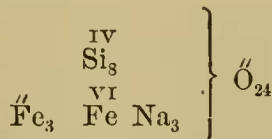
Composition :

			Oxygen.		
SiO$_2$	=	49.83	26.409		
TiO$_2$	=	1.43	0.558	27.164	5.702
ZrO$_2$	=	0.75	0.197		
Al$_2$O$_3$	=	trace			
Fe$_2$O$_3$	=	15.88	4.764	4.764	1.000
FeO	=	17.95	3.985		
MnO	=	1.75	0.385		
Na$_2$O			2.149	6.928	1.454
LiO	=	8.33			
K$_2$O	=	1.44	0.245		
MgO	=	0.41	0.164		
Ignition	=	0.20			

97.97

$\ddot{R} : \dddot{R} : \dot{R} = 17 : 3 : 4.3$

To obtain the atomic ratio, we have :

Si =   0.836

Ti =   0.017   Si =   0.0095   Quotient. Atoms.

Zr =   0.006   Si =   0.0020   Si =   0.8475   8.56

Fe =   0.099   Fe =   0.099   1.00

Fe =   0.249   Fe =   0.278   2.809

Mn =   0.025   Na =   0.286   2.88

Na =   0.268   O   =   2.428   24.52

K   =   0.031   Na =   0.018

Mg =   0.010   Fe =   0.004

O   =   2.428

and the nearest symbol will be

$$\left. \begin{array}{c} \overset{\text{IV}}{\text{Si}}_3 \\ \overset{''}{\text{Fe}}_3 \ \overset{\text{VI}}{\text{Fe}} \ \text{Na}_3 \end{array} \right\} \overset{''}{\text{O}}_{24}$$

It is apparent that neither the oxygen ratio, nor the atomic ratio lead to a very satisfactory formula, in as much as the formula given contains one-half atom of oxygen more than required to satisfy the affinities of the metals.

Owing to the extreme cleavage of the mineral, a sufficiently thin section could not be prepared to allow a microscopical and optical examination ; and the presence or absence of minute particles of other species could therefore not be ascertained.   The analysis was conducted with great care, of every constituent a check determination was obtained.   Three alkali determinations gave identical results.   Only the ferrous iron was but once determined.   After being in sealed tube for nearly a week, the mineral was not completely decomposed.   After titration I filtered from silica and undecomposed part, removed silica by sodium hydrate, and from the weight of residue I calculated the ferrous iron pro toto.   In the face of the duplicate and closely agreeing determinations I cannot explain the deficiency of two per centum in the analysis.

3. ZIRCON.

Occurs in brilliant, mostly iron black crystals, imbedded in quartz or in astrophyllite.   The size varies from microscopic dimensions to $\frac{1}{4}$ inch pyramidal edge.

Crystallographical properties.   The form is a combination P. ∞P. 0P. I observed the basal plane on every crystal which I examined.   It is sometimes very small, but mostly very plainly developed and splendent.   On one crystal it appeared distinctly rhomboid, and this induced me to measure the angles of the pyramidal edge, which I found 120° 56′ ; 123° 15′.   But all other crystals gave as nearly 123° as the uneven faces could be expected to average.   The rhomboidal crystal stands, therefore, alone as a distorted individual.   The prism is generally very small, often only a splendent edge.

When boiled with strong hydrochloric acid the black color disappears, and the substance exhibits a yellowish flesh color.   The individuals appear corroded.   Otherwise, physical characters identical with those of other localities.

Specific gravity at 12 C$^\circ$ = 4.538.

Composition :

$$\begin{array}{lcl}
SiO_2 & = & 29.70 \\
ZrO_2 & = & 60.98 \\
Fe_2O_3 & = & 9.20 \\
MgO & = & 0.30 \\
\hline
& & 100.18
\end{array}$$

The coarse powder of the mineral had been boiled for some time with strong hydrochloric acid, until no more iron was dissolved.   The unusually large percentage of iron still shown by the analysis must reasonably be considered as belonging to the mineral.

NOTE.—While this paper is in press, I obtained other specimens from El Paso County, in which a black mica occurs in large foliated masses, traversed by astrophyllite.   This and another mineral, apparently arfvedsonite changed into a micaceous mineral, I am investigating at present.